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Bismuth oxide nanoparticles in the stratosphere

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Abstract. Platey grains of cubic Bi_2O_3, α-Bi_2O_3, and $Bi_2O_{2.75}$ nanograins were associated with chondritic porous interplanetary dust particles W7029C1, W7029E5, and 2011C2 that were collected in the stratosphere at 17–19 km altitude. Similar Bi oxide nanograins were present in the upper stratosphere during May 1985. These grains are linked to the plumes of several major volcanic eruptions during the early 1980s that injected material into the stratosphere. The mass of sulfur from these eruptions is a proxy for the mass of stratospheric Bi from which we derive the particle number densities (p m^{-3}) for "average Bi_2O_3 nanograins" due to this volcanic activity and those necessary to contaminate the extraterrestrial chondritic porous interplanetary dust particles via collisional sticking. The match between both values supports the idea that Bi_2O_3 nanograins of volcanic origin could contaminate interplanetary dust particles in the Earth's stratosphere.

Introduction

The presence of cosmochemically volatile elements such as Bi, Tl, and Hg in extraterrestrial materials has long been considered a cornerstone for models of solar system evolution [*Woolum et al.*, 1978] and thus a fundamental criterion for evidence of late-stage solar nebula processing. In general, these marker elements are extremely rare in terrestrial and lunar rocks and, while present in meteorites, are only detected in significant amounts using bulk analytical methods in carbonaceous chondrites and unequilibrated ordinary chondrites. Both Bi and Hg have been observed in mineral forms in ultrafine-grained solar system materials, viz., HgS associated with a carbonate grain in the Orgueil CI carbonaceous chondrite meteorite [*Mackinnon and Kaser*, 1990] and cubic Bi_2O_3 in chondritic porous (CP) interplanetary dust particle (IDP) W7029C1 collected in the stratosphere [*Mackinnon and Rietmeijer*, 1984]. *Mackinnon and Rietmeijer* [1984] considered, but rejected, the possibility of stratospheric contamination of this IDP by submicron Bi_2O_3 grains on the grounds that (1) collision frequencies for particles in very low abundance are probably too low to interact with IDPs in the stratosphere and (2) the low abundance of Bi_2O_3 grains in this extraterrestrial particle was consistent with solar nebula condensation models. A study of stratospheric dust levels at ambient natural conditions by *Zolensky and Mackinnon* [1985] supported that IDP contamination by dusts >100 nm in diameter was unlikely owing to relatively short stratospheric residence times. Since 1984, additional data have been obtained on the mineralogy and chemistry of a wide range of solid (sub)micrometer stratospheric dusts such as volcanic silica shards, "silicate" clusters, and ash particles [*Rietmeijer*, 1988, 1992, 1993a; *Zolensky et al.*, 1989]. These recent data, and new observations on Bi oxides in IDPs reported in this paper, set the stage to re-assess the origin of these nanograins in the stratosphere.

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There is a growing awareness that studies of submicrometer mineral dusts in the stratosphere cannot fully rely on comparisons with the geological database on mineral occurrences. This database typically does not include submicron mineral occurrences. For example, the recovery of submicron rutile grains attached to large (~20 μm in diameter) crystobalite spheres from preindustrial-age Antarctic ice was enigmatic [*Zolensky et al.*, 1988]. Citing the occurrence of these rare grains in two differently located sampling sites, the authors decided on a probable (local) volcanic source in the Antarctic. From geological studies it was not known that submicron Ti oxides can be associated with volcanic ejecta. Similar Ti oxides attached to volcanic silica shards were found in the upper stratosphere [*Rietmeijer*, 1993a]. In terrestrial occurrences, minor submicron mineral grains tend to remain unrecognized. This study contends that contamination of IDPs by stratospheric Bi oxide nanograins is probably due to major volcanic eruptions under nonambient natural conditions. This study does not disclaim an earlier conclusion on the indigenous nature of metallic bismuth in CP IDPs. It builds upon a growing awareness that contamination by stratospheric aerosols compromises the chemical integrity of extraterrestrial particles.

Experiment

This study used (1) published data on CP IDP W7029C1 (allocations W7029*A23; -24) [*Mackinnon and Rietmeijer*, 1984], (2) new data on this particle and CP IDPs W7029E5 and U2011C2 from the NASA Johnson Space Center (JSC) cosmic dust collection, and (3) an upper stratospheric dust collection [*Testa et al.*, 1990]. The NASA JSC cosmic dust program uses inertial-impact collectors mounted underneath the wings of high-flying aircraft for samplings of the dusts in the lower stratosphere at 16.8–19.2 km altitude [*Mackinnon et al.*, 1982]. *Testa et al.* [1990] collected dust in the stratosphere at 34–36 km altitude during May 1985 using a "Battelle" impactor for direct deposition of dust onto transmission electron microscope (TEM) "stacks." A TEM stack consists of Be grids supporting holey carbon thin films that act as dust collectors. We

Table 1. Size, Arithmetic Mean Diameter D_a, Shape Factor F, and Domains of Bi_2O_3 Grains Associated with Three Interplanetary Dust Particles and Three Volcanic Grains in the Upper Stratosphere

Occurrence	Size, nm	D_a, nm	F	Domains
W7029A23/24	379 × 364	254	0.51	yes
	394 × 205*	206	0.29	yes
	419 × 404	281	0.51	rare
	1230 × 770	673	0.32	yes
W7029E5	604 × 190	271	0.165	no
U2011C2	90 × 90	63	0.56	no
	660 × 170	283	0.14	no
"34–36 km"	800 × 350	390	0.23	no
	570 × 329	306	0.31	yes
	546 × 82.5*	244	0.17	yes

$D_a = (a + b + c)/3$, where a, b, and c are particle dimensions with $a > b > c$, $F = (b + c)/2a$.
*Half width along the basis of a triangular grain.

used a Jeol 2000 FX analytical electron microscope (AEM) equipped with a Tracor-Northern TN5500 energy dispersive spectrometer for in situ analysis of elements with atomic number >11 with a ~20 nm probe. The AEM was also used for identification of Bi oxide grains in ultrathin sections of IDPs U2011C2 and W7029E4 supported by holey carbon thin films during analyses. Phase identifications rely on a combination of energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED) analyses. The SAED patterns were calibrated using a Au-coated holey carbon film that was analyzed under identical conditions as the particles. The interplanar spacings were determined with a relative error of ~2%. Grain sizes were measured with a ~10% relative error on calibrated TEM negatives.

Observations

Bismuth oxides were associated with three different CP IDPs collected in the lower stratosphere (Tables 1 and 2). The IDP U2011C2 contains a platey angular subequant grain (90 × 90 × 10 nm) and thin elongated grain (660 × 170 × 20 nm) (Figure 1). Both single-crystal grains show dislocation substructures. The SAED data for the largest grain indicate epitaxially related monoclinic α-Bi_2O_3 and tetragonal β-Bi_2O_3 phases. In particle W7029E5 a thin (10 nm) angular grain (604 × 190 nm) is a monoclinic α-Bi_2O_3 single crystal. In addition to the three platey Bi_2O_3 grains in W7029C1 previously reported by *Mackinnon and Rietmeijer* [1984], we located an additional Bi oxide grain. The transparent matrix of this grain (1230 × 770 × 20 nm) contains several (subcircular opaque domains, 95 × 95 nm to 135 × 86 nm in size. Reexamination of the previously reported Bi oxide grains revealed similar domains that are 18–42 nm in diameter. Three platey angular bismuth grains were collected in the stratosphere between 34 and 36 km altitude during May 1985 (Tables 1 and 2) [*Rietmeijer*, 1993a]. One grain (800 × 350 × 20 nm) is a single crystal of α-Bi_2O_3, although the available SAED data cannot exclude that this grain is not $Bi_2O_{2.73}$ or $Bi_2O_{2.75}$. These latter oxides are metastable phases that may form during oxidation of BiO to Bi_2O_3 [*Zav'yalova and Imamov*, 1968]. The other grains have a rectangular (570 × 329 × 20 nm) and a triangular shape (165 (half width) × 546 × 20 nm). Both grains have opaque domains in a transparent matrix (Figure 2). The domains are (sub)circular (40–140 nm in diameter) and elongated, 100 × 50 nm up to 200 × 150 nm in size.

Discussion

The NASA JSC cosmic dust program is a rich source of materials for stratospheric research [*Mackinnon*, 1986]. Contamination of IDPs in the stratosphere was documented for volcanic silica shards (<0.45 μm in size) [*Rietmeijer*, 1988], KCl, and Na-K-S-Cl-Br-rich aerosols [*Rietmeijer*, 1993b, 1995], sulfur [*Mackinnon and Mogk*, 1985], and iron [*Jessberger et al.*, 1992]. Contamination has received considerable attention in studies of IDPs. Extraneous dust is generally not a problem during preflight and postflight handling of collector surfaces, and it is negligible and recognizable during AEM analyses [*Rietmeijer*, 1993a]. The possibility that IDPs on a collector become contaminated with particles collected at a later date remains, but *Flynn* [1994] showed that these events have a very low probability. Contamination as a result of particle migration within the viscous capture medium on the collector surface is unlikely.

The average dimensions of Bi_2O_3 grains listed in Table 1 are 570 × 295 × 20 nm. For a density of 8.8 g cm^{-3} (ρ = 8.2 g cm^{-3} for cubic Bi_2O_3; ρ = 9.37 g cm^{-3} for monoclinic α-Bi_2O_3), the "average Bi_2O_3 nanograin" contains 1.3×10^{-14} g of Bi. The domain texture (Figure 2) is density contrast. For example, crystalline domains in an amorphous matrix have a higher density than the matrix, or cubic Bi_2O_3 relics due to an incomplete polymorphic transition to monoclinic α-Bi_2O_3 at 710°C [*Zav'yalova et al.*, 1965] with kinetically controlled β-Bi_2O_3 formation [*Sillén*, 1937].

The gravitational settling of these platey Bi_2O_3 nanograins can be calculated using the Stokes-Cunningham fall law [*Kasten*, 1968]. The residence times for settling from 20 to 17 km range from 1 to 7 months. Particles in this size range settle in the stratosphere under the influence of gravity and diffuse in the vertical direction [*Turco et al.*, 1979]. The eddy diffusion

Table 2. Temporal Relationships Among NASA JSC Cosmic Dust Collectors at 16.8–19.2 km Altitude From 1980 to 1985, the Eruptions of Mount St. Helens, El Chichón, and Nyamuragira (Source of the Mystery Cloud) Volcanos, and a Sampling of the Stratosphere Between 34 and 36 km Altitude

	Date
U2–9*	March 1976
Mount St. Helens eruption	May 18, 1980
Alaid eruption	April 27, 1981
Pagan eruption	May 15, 1981
W7013	May 22 to July 6, 1981
W7017*	July 17 to Sept. 15, 1981
W7027/W7029†	Sept. 15 to Dec. 2, 1981
"Mystery Cloud"	early 1982
U2001	March 13 to April 8, 1982
El Chichón eruption	March 28 to April 4, 1982
U2011†	March 15 to April 1, 1983
U2015	June 22 to Aug. 18, 1983
U2024*	Sept. 30, 1983 to July 13, 1984
U2022	April 9 to June 26, 1984
"34–36 km"	May 1985
U2034	April 17 to Aug. 28, 1985

Data are from *Rietmeijer and Warren* [1994] unless noted otherwise.
**Zolensky et al.* [1989].
†Samples with IDPs containing Bi_2O_3 nanograins.

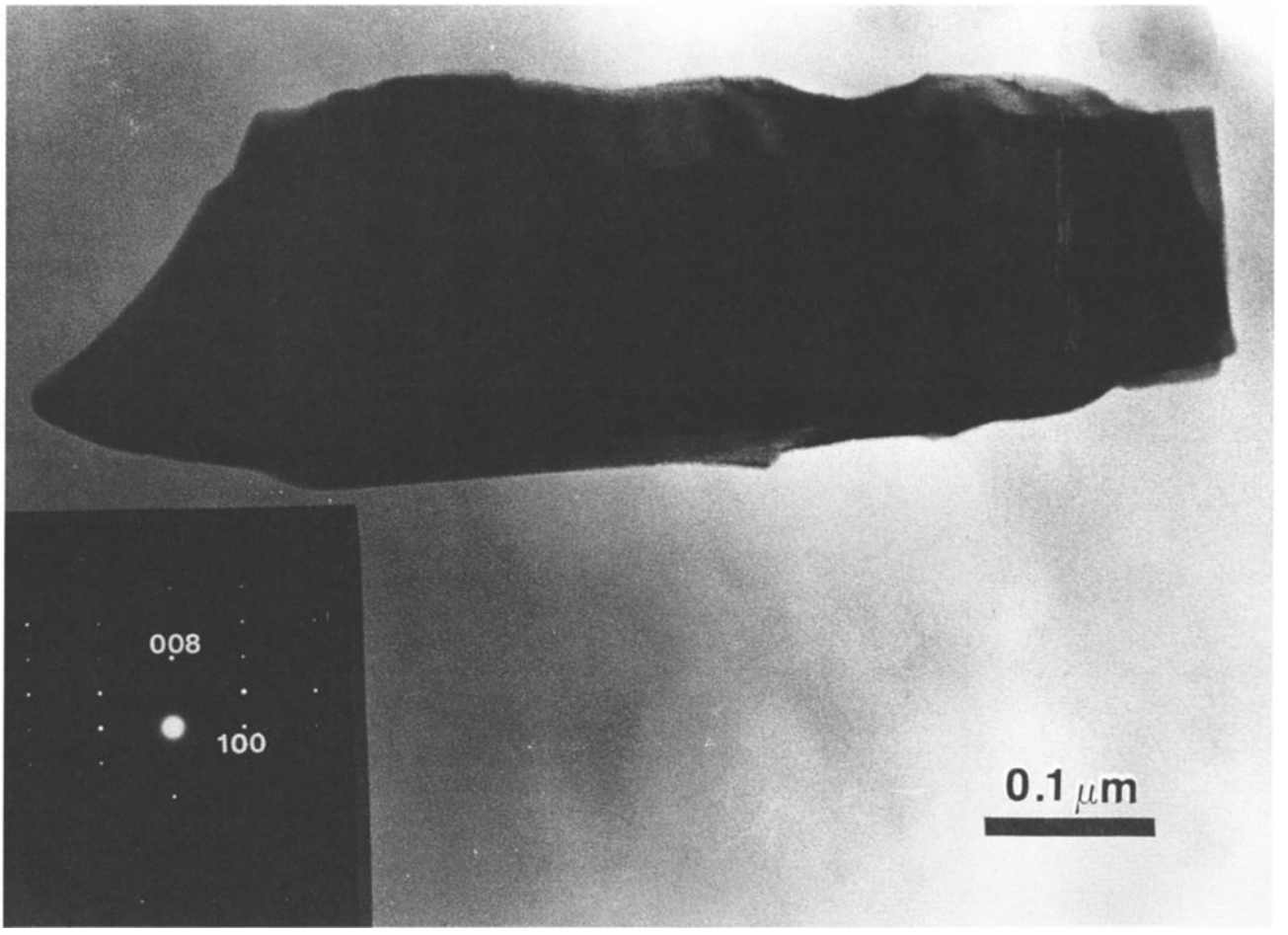

Figure 1. Angular bismuth oxide grain associated with CP IDP U2011C2. The grain is viewed along the crystallographic *b* axis of the tetragonal $Bi_2O_{2.73}$ single-crystal grain. The gray background is the epoxy of the ultrathin section wherein this particle is embedded.

coefficients increase as a function of increasing altitude in the stratosphere [*Turco et al.*, 1979]. Vertical turbulent diffusion [*Thomas et al.*, 1984] and other nongravitational forces (e.g., photospheric lofting, electrical forcing) further increase the stratospheric residence time of the Bi_2O_3 nanograins. The anthropogenic or volcanic nanograin contaminants of CP IDPs were present on the IDPs prior to their collection.

Bismuth has a wide range of industrial applications, but it is not typically associated with anthropogenic activities that are sufficiently energetic to inject quantities of Bi oxides into the stratosphere. Bismuth metal is used in propulsion and auxiliary power supplies in spacecraft [*Rosenblum*, 1963]. Thirty Bi and Bi,Cl grains (1–3 μm in size) associated with penetration holes in space-facing surfaces of the Solar Maximum satellite in orbit from February 14, 1980, to April 12, 1984, confirmed the presence of Bi-rich grains in space [*Rietmeijer et al.*, 1986]. A fraction of these orbiting grains could have reentered the atmosphere, but their very small size will limit their ability to radiate thermal energy [*Rizk et al.*, 1991]. Hence survival during atmospheric entry is dubious. There is no evidence that high amounts of reentered Bi nanograins were present in the stratosphere during the period of interest here (Table 2). The Bi_2O_3 nanograins that contaminated CP IDPs in the stratosphere were most likely related to volcanic eruptions that are common sources for Bi into the atmosphere. A problem with this source link is that, as far as we are aware, samplings of distal volcanic airfall deposits and plumes have not (yet) found these nanograins. This situation can exist because these ejecta do not receive the same scrutiny on the nanometer scale as the extraterrestrial particles.

Bismuth from fumarolic volcanic gases add a global flux of 4000 tons Bi/yr to the atmosphere, which is overwhelmingly responsible for the global bismuth reservoir in the atmosphere [*Patterson and Settle*, 1987]. The Bi enrichment factor was among the highest of volatile metals in condensates, sublimates (gas phase), and incrustations of the Merapi Volcano [*Symonds et al.*, 1987]. Above ~500°C, PbS and BiS are the thermodynamically stable gas species, and bismuth is associated with galena (Pb/Bi = 1.3–1.5); around this temperature, BiCl also becomes a stable gas species, while $BiCl_3$ is stable between 100 and 500°C [*Symonds et al.*, 1987]. Eruption plume samples of Mount St. Helens included abundant (Na, K)Cl cubes containing some amounts of Zn, Cd, Fe, and Cu [*Varekamp et al.*, 1986]. At high temperatures these metals formed chlorides or elemental (Zn and Cd) gas species [*Symonds et al.*, 1987]. The enrichment factors for Bi, Zn, Cd, and Cu are also among the highest of metals in volcanic aerosols [*Pennisi et al.*, 1988]. Many vapor phase metals are scavenged efficiently by small particles of elemental sulfur in volcanic plumes [*Patterson and Settle*, 1987], but bismuth may not show this behavior [*Hinkley*, 1991]. A listing of bismuth minerals includes Bi oxides but not Bi chlorides [*Angino and Long*, 1979] that may not exist as

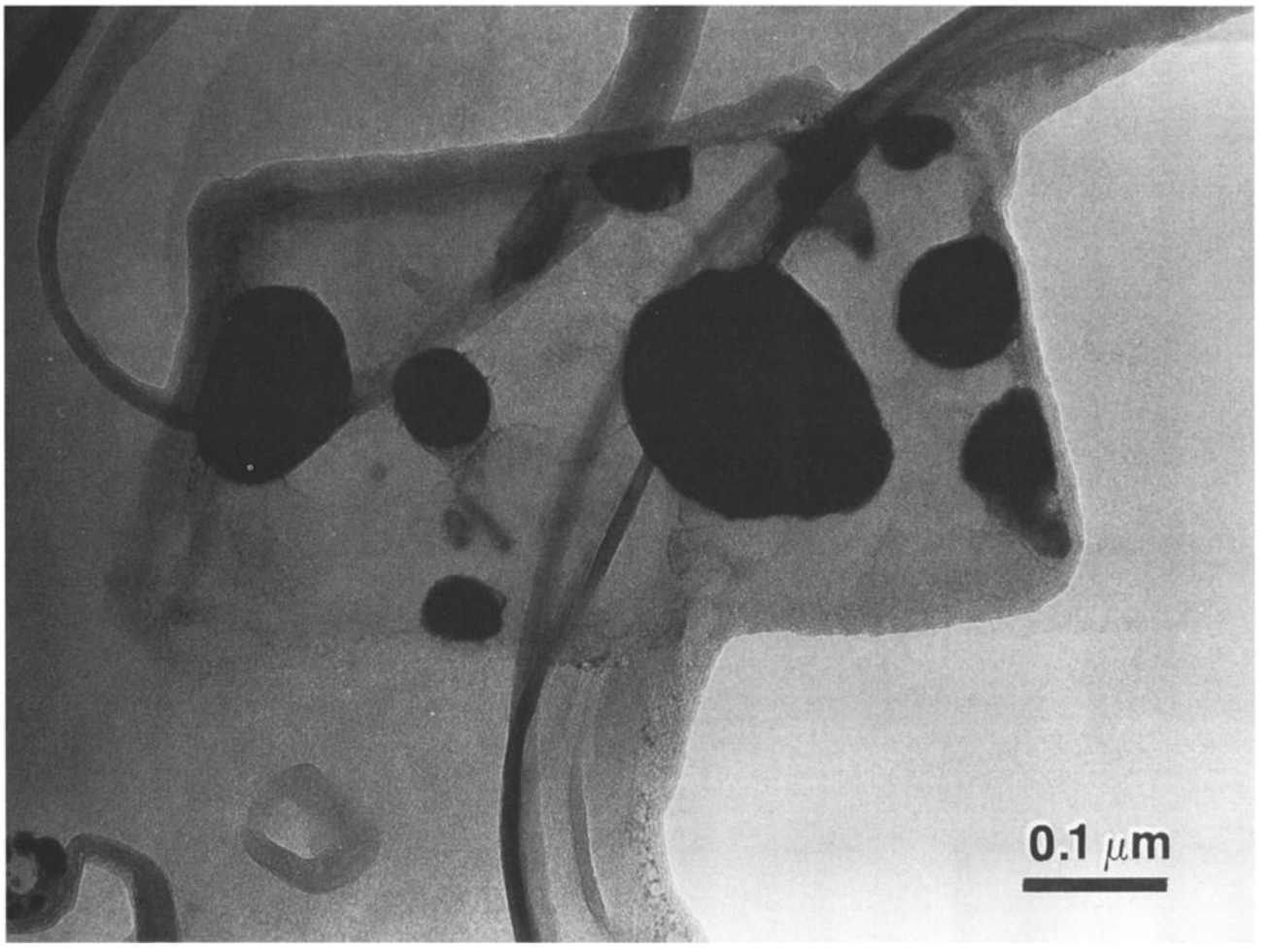

Figure 2. Domains in the matrix of an angular Bi oxide nanograin collected in the stratosphere between 34 and 36 km altitude during May 1985. The grain is supported by a holey carbon thin film during TEM and AEM analyses.

stable mineral phases. Its gas species are probably oxidized to stable oxides, viz., $2BiCl_3$ (g) + $3H_2O$ (g) = Bi_2O_3 + 6HCl (g) or, associated with halite (NaCl) of sylvine (KCl), as $2NaCl \cdot BiCl_3 + H_2SO_4$ (l) + $3H_2O$ (g) = $Bi_2O_3 + Na_2SO_4$ + 8HCl (g). The latter is reminiscent of the role played by ~1-μm-sized halite cubes in the observed increase of HCl gas in the stratosphere 1 month after eruption of the El Chichón volcano [*Woods et al.*, 1985]. We note that thin films of Bi-O are prepared by distilation of Bi_2O_3 powders at 6.5×10^{-8} atm onto cleavage faces of NaCl crystals at room temperature up to 350°C [*Zav'yalova et al.*, 1965].

The annual sulfur flux is a proxy for this flux of Bi to the atmosphere as Bi/S = $\sim 2.1 \times 10^{-4}$, which yields 4000 tons Bi/yr [*Patterson and Settle*, 1987]. The sulfur flux was based on fumarolic SO_2 emissions during quiescent activity. The SO_2 flux in quiescent volcanic plumes is 140–1350 tons/d. The plume SO_2 concentrations are diluted in the atmosphere by factors of up to 10^5 compared to the concentrations in fumarolic gases [*Casevall et al.*, 1984]. Finally, during July and August 1980, debris of the Gareloi volcano (Alaska) reached an altitude of 19.2 km, which was about twice the height of its visible eruption clouds. *Sedlacek et al.* [1981] suggested that remote volcanic activity contributes to an "ambient" stratospheric aerosol background. None of these diffuse reservoirs is likely add significant amounts of Bi to the stratosphere. Only volcanic ejecta plumes that penetrate the tropopause can be a viable source of Bi_2O_3 nanograins with high enough concentrations in stratosphere to contaminate IDPs by collisional sticking during periods of frequent explosive volcanism [*Lepel et al.*, 1978; *Symonds et al.*, 1990].

Considerable volcanic activity during the early 1980s included major eruptions of the Mount St. Helens (United States), Alaid (Kamchatka), Pagan (Kuril Islands), El Chichón (Mexico), and Nyamuragira (Zaire) volcanos (Table 2). The last volcano was the source of the "Mystery Cloud" over the northern hemisphere in early 1982. Long-term monitoring of stratospheric aerosols from 1974 to 1987 at Mauna Loa (Hawaii) and in Hampton (Virginia) showed a flat aerosol level prior to eruption of Mount St. Helens volcano and a sudden increase due to its eruption. The elevated aerosol level that existed between this eruption and the arrival of aerosols from the Mystery Cloud and El Chichón volcano was greatly increased owing to aerosols from these two sources. In 1985 the aerosol level had not yet decayed to the early 1980 level [*McClelland et al.*, 1989]. The Mystery Cloud aerosols occurred over Garmisch-Partenkirchen (Germany) at >30 km altitude during 1982 and early 1983 along with other volcanic aerosols between 10 and 30 km altitude [*McClelland et al.*, 1989]. It is not surprising that sample U2024 (Table 2) contained a high amount of volcanic "silicate" dusts (1–5 μm in size) in the

Table 3. Mass of S Injected Into the Stratosphere by the Mount St. Helens, Nyamuragira (Source of the Mystery Cloud), and El Chichón Volcanic Eruptions, the Derived Mass of Stratospheric Bi Using Bi/S = $\sim 2.1 \times 10^{-4}$, and the Corresponding Number of "Average Bi_2O_3 Nanograins" and Their Number Density in the Stratosphere

	Mount St. Helens	Mystery Cloud	El Chichón
S (g)	1.2×10^{12}	5.6×10^{12}	1.7×10^{13}
Bi (g)	2.5×10^{8}	5.9×10^{8}	1.75×10^{9}
Bi_2O_3	1.9×10^{22}	4.5×10^{22}	1.3×10^{23}
Number density, p m^{-3}	2.6×10^{3}	6.0×10^{3}	1.7×10^{4}

	W7029C1	W7029E5	U2011C2	"34–36 km"
Number density,* p m^{-3}	9.3×10^{5} 5.1×10^{5}†	1.3×10^{6}	5.9×10^{5}	1.0×10^{4}

See text for references and for explanation for derivation of the mass of stratospheric Bi.

*Number density of Bi oxide nanograins in the stratosphere calculated from their abundances on three CP IDPs and measured in the stratosphere between 34 and 36 km altitude during May 1985.

†Number density value assuming that this IDP was from a cluster particle that broke apart during collection (see text).

lower stratosphere ~40 months after the El Chichón eruption [*Zolensky et al.*, 1989]. A year later, nanometer-sized volcanic dusts from its 1982 eruption were present between 34 and 36 km altitude (Table 2). At this altitude the observed number density for grains (90–500 nm in diameter) was 5.0×10^5 particles per cubic meter (p m^{-3}) [*Testa et al.*, 1990]. Platey Bi oxide nanograins accounted for 2% of these particles, or 1.0×10^4 p m^{-3} [*Rietmeijer*, 1993a].

The eruptions of Mount St. Helens and El Chichón volcanos and the Mystery Cloud injected large amounts of aerosol into the stratosphere between May 1980 and April 1982 [*Evans and Kerr*, 1983]. The El Chichón plume reached 26 ± 3 to 33–35 km altitude [*Coulson et al.*, 1982; *Woods and Self*, 1992]. On May 18, 1980, the Mount St. Helens plume reached 23 km altitude, and eruptions during June, July, August, and October 1980 penetrated the tropopause [*Sedlacek et al.*, 1983]. The sulfate residence time is 11.2 ± 1.2 months, and prior to the Alaid and Pagan volcanic eruptions, the sulfate aerosol loading of the stratosphere started to decline in April 1981 [*Sedlacek et al.*, 1983]. During July 1981, the sulfate aerosol concentration peaked at 2.83 ppbm, i.e., 1.1×10^5 tons of S (at 20 km altitude; mass of the stratosphere <30 km is 8.48×10^{20} g), but declined to 1.48 ppbm during collection of IDPs W7029C1 and W7029E5 [*Sedlacek et al.*, 1983].

Using SO_2 [*Evans and Kerr*, 1983] plus sulfate [*Sedlacek et al.*, 1983] data, and the ratio Bi/S = $\sim 2.1 \times 10^4$, the sulfur mass ejected by the Mount St. Helens eruption supports 2.6×10^3 average Bi_2O_3 nanograins per cubic meter (Table 3). Including sulfate data for the Alaid and Pagan volcanic eruptions (4.4×10^3 p m^{-3}) during the period prior to the eruption of El Chichón, we obtained 7.0×10^3 p m^{-3} average Bi_2O_3 nanograins in the stratosphere. Similarly, from the ejected mass of SO_2, we calculated 2.3×10^3 average Bi_2O_3 nanograins per cubic meter due to the El Chichón volcano and the Mystery Cloud (Table 3).

Contamination of IDPs in the stratosphere occurs via collisional sticking. The collision frequency z that can be calculated by $z = n4\pi r^2 c$, where n is the number of particles per cubic meter (p m^{-3}), r the average particle radius (m) (here $0.5D_a$), and c the average velocity (m s^{-1}). Since individual IDPs range in size from ~10 and ~50 μm, and still larger, possibly up to 100 μm, for cluster particles [*Rietmeijer and Warren*, 1994], we prefer not to consider Brownian coagulation. The settling velocity and stratospheric residence time of an IDP can be calculated from its dimensions and density [*Rietmeijer*, 1993b, 1995]. The value of z is obtained from the number of Bi_2O_3 nanograins associated with an IDP and its residence time (Tables 1 and 4). Substitution of the appropriate parameters for an IDP yielded the number of Bi_2O_3 nanograins in the stratosphere when the IDP fell through the stratosphere (Table 3). About 1.0×10^6 average Bi_2O_3 nanograins per cubic meter (September 15 to December 2, 1981, and 5.9×10^5 p m^{-3} (March 15 to April 1, 1982) were present in the stratosphere (Tables 2 and 3). Considering the uncertainties, the results

Table 4. Dimensions, Arithmetic Mean Diameter D_a, Shape Factor F, Density ρ, Calculated Gravitational Settling Velocity V, and Stratospheric Residence Time t for Three CP IDPs

IDP	Size, μm	D_a, μm	F	ρ, g cm^{-3}	V, m s^{-1}	t, days
W7029C1*	$12 \times 8.5 \times 6.5$	9	0.63	0.36	7.4×10^{-4}	266
	$60 \times 60 \times 60$	60	1.0	0.01	1.3×10^{-3}	267
W7029E5	$7 \times 4 \times 2$	4.3	0.43	1.8	6.2×10^{-4}	241
U2011C2	$9 \times 9 \times 6$	8.0	0.83	0.45	9.2×10^{-4}	214

The largest dimensions are from the NASA JSC cosmic dust catalogs. The smallest dimension is a best estimate based on morphology.

*W7029C1 is the parent of allocations W7029A23/24. It is part of a cluster particle estimated at 60 μm in diameter. The density is obtained from a relationship between fractal IDP size and density, ρ (g cm^{-3}) = 1.37×10^8 (size (nm))$^{-2.17}$ [*Rietmeijer*, 1993c].

show a close match between the number densities of Bi_2O_3 nanoparticles based on the mass of stratospheric bismuth, and those required for contamination of CP IDPs (Table 3), in particular, for the link between the Mystery Cloud and El Chichón eruption and CP IDP U2011C2, and the nanograins in the upper stratosphere during May 1985. The number of average Bi_2O_3 nanograins from eruptions of the Mount St. Helens, Alaid, and Pagan volcanos are too low for contamination of CP IDPs W7029C1 and W7029E5. However for the cluster particle that included W7029C1 the number of calculated contaminant particles, 1.1×10^4 p m^{-3}, matches well with the average Bi nanograins inferred from the mass of stratospheric Bi. We note that IDP U2022C2 is also part of a larger cluster particle. This result is somewhat fortuitous; that is, our AEM analyses indentified all contaminant nanograins in these cluster particles. We submit that Bi_2O_3 nanograins of volcanic origin due to oxidation of $NaCl \cdot BiCl_3$ in ejecta plumes are injected into the stratosphere in sufficient numbers to collide with, and contaminate, CP IDPs in the stratosphere. During periods of major volcanic activity, the amount of stratospheric Bi (using the mass of sulfur as a proxy) was sufficiently large, and residence times of platey Bi_2O_3 nanograins were long enough, to contaminate CP IDP cluster particles settling in the stratosphere.

Conclusions

Platey nanograins of cubic Bi_2O_3, α-Bi_2O_3, and $Bi_2O_{2.75}$ (or $Bi_2O_{2.73}$) were associated with three CP IDPs collected in the lower stratosphere between 17 and 19 km altitude during fall 1981 (W7029C1, W7029E5) and late March 1983 (U2011C2). Similar nanograins were present between 34 and 36 km altitude during May 1985. The platey grains, $63 < D_a$ (nm) < 673, were formed in volcanic ejecta plumes. The Bi_2O_3 grains formed by oxidation of $NaCl \cdot BiCl_3$ cubes in ascending plumes. The mass of stratospheric sulfur from several major volcanic eruptions during the early 1980s is a proxy for the mass of stratospheric Bi. We assumed that all Bi was present as average Bi_2O_3 nanograins. The amounts of nanograins due to this volcanic activity show a good match with the stratospheric Bi_2O_3 abundances required to contaminate extraterrestrial CP IDPs via collisional sticking. These Bi_2O_3 nanograins will be present on all IDPs from the samples listed in Table 2.

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